Field portable time resolved SORS sensor for the identification of concealed hazards

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ABSTRACT

Raman spectroscopy, when used in spatially offset mode, has become a potential tool for the identification of explosives and other hazardous substances concealed in opaque containers. The molecular fingerprinting capability of Raman spectroscopy makes it an attractive tool for the unambiguous identification of hazardous substances in the field. Additionally, minimal sample preparation is required compared with other techniques. We report a field portable time resolved Raman sensor for the detection of concealed chemical hazards in opaque containers. The new sensor uses a pulsed nanosecond laser source in conjunction with an intensified CCD detector. The new sensor employs a combination of time and space resolved Raman spectroscopy to enhance the detection capability. The new sensor can identify concealed hazards by a single measurement without any chemometric data treatments.

Keywords: Time resolved SORS, Raman spectroscopy, explosive precursors, non-contact analysis, forensic analysis, homeland security.

1. INTRODUCTION

Raman spectroscopy has emerged as a potential tool for the detection and identification of explosives [1]. Raman can be used in the non-invasive detection of explosives with excellent chemical specificity compared to other spectroscopic techniques. Recent developments indicate that Raman spectroscopy can be used for depth profiling through diffuse containers at close range and standoff distances[2, 3].

Spatially Offset Raman spectroscopy pioneered by Matousek et. al.[4] is a methodology where the Raman photons are collected at an offset from the point of excitation. SORS has paved the way to depth profiling through diffuse containers and is reported extensively in literature.[5, 6, 7]Raman spectroscopic measurements made in the time domain minimises the adverse effects of fluorescence. Time resolved Raman spectrometers use a pulsed laser as excitation source and time gated camera for the detection of Raman photons. Raman scattering is instantaneous on the other hand fluorescence

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occurs with time constant of picoseconds to several nanoseconds depending on the molecular structure of the target compound. By synchronizing the opening of detector with the excitation pulse, fluorescence can be rejected or minimised[8]. The time resolved measurements also help to reject the ambient light making the system most suitable for field applications. Depth profiling can be accomplished with the help of time resolved Raman spectroscopy. Depth profiling using time resolved Raman requires laser systems with pulse duration of the order of picoseconds to provide the necessary time resolution[9]. Depth profiling by a combination of these technique using a picosecond pulsed laser system has also been reported[10].

By combining the principles of spatial and time resolved Raman, the complexity in instrumentation can be greatly reduced. In this work we describe a combined space and time resolved Raman instrumentation for depth profiling through diffuse containers. This spectrometer uses a nanosecond laser system to detect explosive precursors inside diffuse plastic containers. The developed spectrometer can detect explosive precursors inside diffuse opaque containers with a single measurement.

2. METHOD

A detailed description of the time resolved spectrometer has been reported earlier [2]. A schematic diagram of the Raman spectrometer is shown in Figure 1.The excitation source is a nanosecond pulsed (10Hz) laser system with output pulse energies of the order of 7 mJ. An axicon lens was used to produce the required offset between the excitation and detection zones. The energy density on the surface of the sample container was measured to be 1.5 mJ/ cm^2 which is equivalent to an average power of 15 mW. The Raman photons were collected by a one to one imaging system consisting of two identical biconvex lenses 6 cm in focal length. The collected Raman photons were coupled into a fibre bundle and delivered to a grating spectrometer. A gated ICCD camera connected at the output slit of the spectrometer was used to detect the Raman photons.

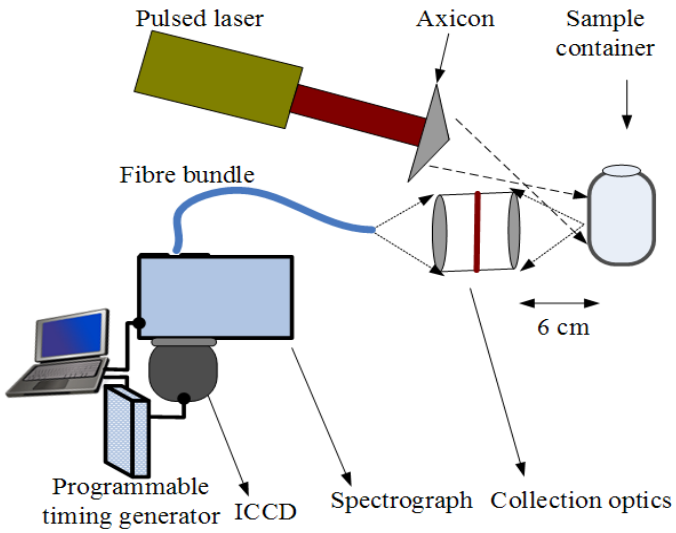

Figure 1. Schematic diagram of the time and space resolved Raman spectrometer.

For our measurements the gate width was set at 4 nanoseconds and the gate delay was varied gradually. The samples were placed at a distance of 6 cm from the collection optics as shown in Figure 1

2.1 Time resolved SORS measurements

The time resolved measurements were carried out under fluorescent light background inside our laboratory. Explosive precursors were concealed inside white as well as highly fluorescing coloured high density polyethylene (HDPE) containers of wall thickness up to 2 mm. The sample containers were placed at a distance of 6 cm from the collection optics and the detector gate delay was optimised to get an interference-free spectrum of the concealed substance. The average acquisition time for a single measurement was 50 seconds (100 pulses, 5 acquisitions). The reference spectra of the chemicals were obtained by placing pure samples inside a clear plastic clip seal bag and collecting the spectrum in direct Raman geometry.

3. RESULTS AND DISCUSSIONS

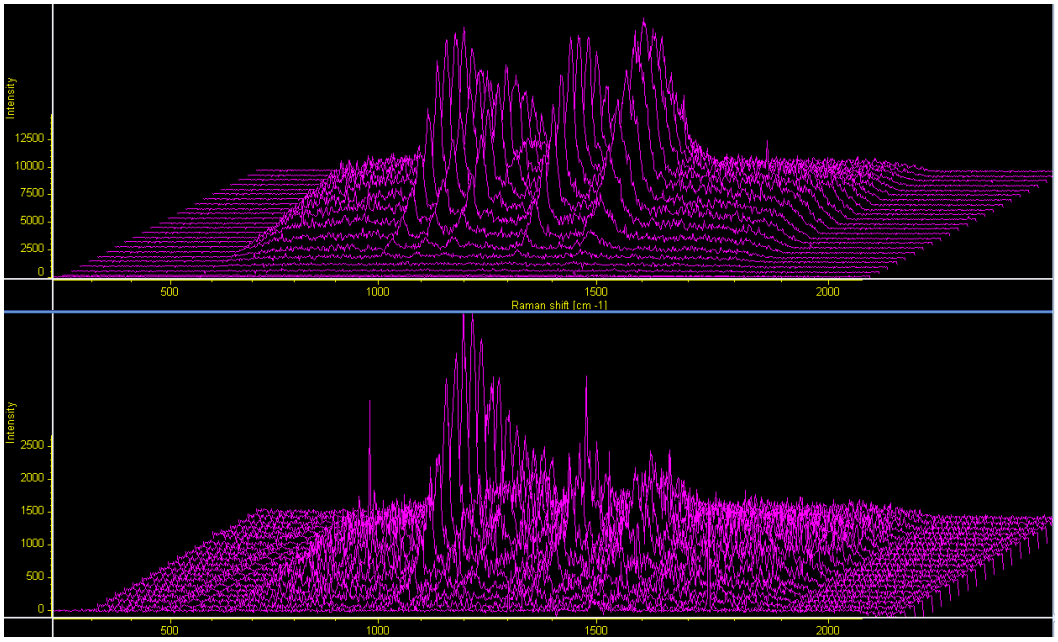

Figure 2 Time resolved spectral measurement of Barium sulphate concealed inside HDPE container. Top subplot indicates a direct Raman measurement and the bottom subplot illustrate a time-resolved SORS measurement.

Figure 2 illustrate the basic concept of time resolved SORS measurements. Top subplot in Figure 2 corresponds to a time resolved measurement with a gate width of 4 nanoseconds. The gate delay was varied from 127 to 150 nanoseconds making a spectral measurement every one nanosecond interval. As evident from the figure, the spectra is a combination of container and sub layer peaks which made the identification of the concealed substance not possible. The bottom subplot of Figure 2 illustrates a spectral measurement after introducing a spatial offset of approximately 7 mm to the illumination using an axicon lens and changing the detector gate delay at constant intervals of 55 picoseconds. By creating an offset between the excitation and detection zones, the relative contributions of the surface and sub-layer

within the collected spectrum changes where the barium sulphate spectral line becomes of high significant intensity when compared to those lines from the container wall material. Also as the gate delay progresses the contributions from the surface layer peaks decreases sharply till an interference-free spectrum of the sub-layer is acquired. This is further illustrated in Figure 3, for barium sulphate concealed inside red plastic container of 1 mm wall thickness. In Figure 3 the spectral measurement at zero offset shows the combined spectrum of the surface and sub-layer. At 7 mm offset and gate delay of 11 ns, the acquired TR-SORS spectrum revealed the sub layer and complete suppression of the surface layer.

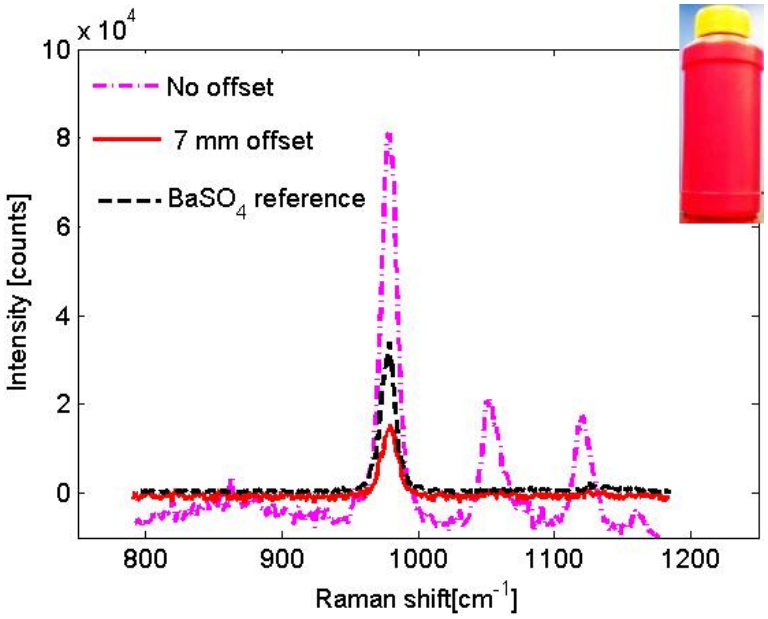

Figure 3 Barium sulphate in side red plastic container detected using a single measurement at 7 mm offset.

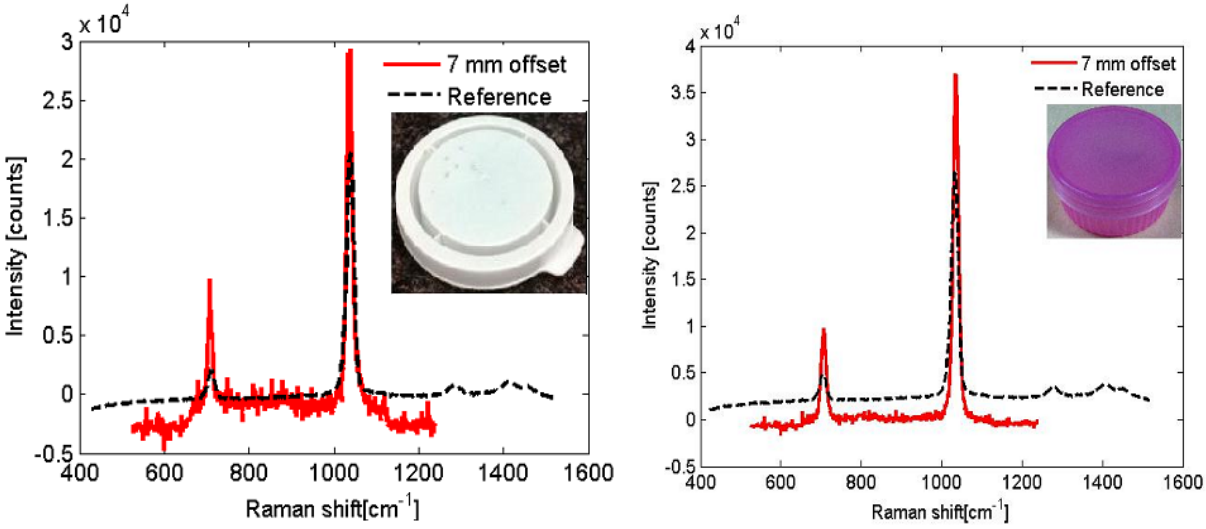

Figure 4 Ammonium nitrate concealed behind white HDPE plastic sheet (a) and pink container (b) detected.

Ammonium nitrate and 2, 4-dinitrotoluene were detected behind different types of diffuse opaque plastics and the results are indicated Figure 4 (a) and (b). In the first case Ammonium nitrate crystals inside a clear clip seal plastic bag was

concealed behind a white HDPE plastic sheet of 2 mm thickness. The result is indicated in Figure 4(a). In the second measurement ammonium nitrate crystals were placed inside a highly fluorescing coloured plastic container. The result is indicated in Figure 4(b). As it can be noticed, the signals from the container wall material were efficiently suppressed and resulting spectrum did not require any further multivariate data treatment to retrieve the native spectrum of the ammonium nitrate content.

DNT (2, 4- dinitrotoluene) was also screened inside the red plastic bottle and the result is indicated in Figure 5. The result indicates an excellent match to the reference spectra and very reliable identification of the explosive precursor.

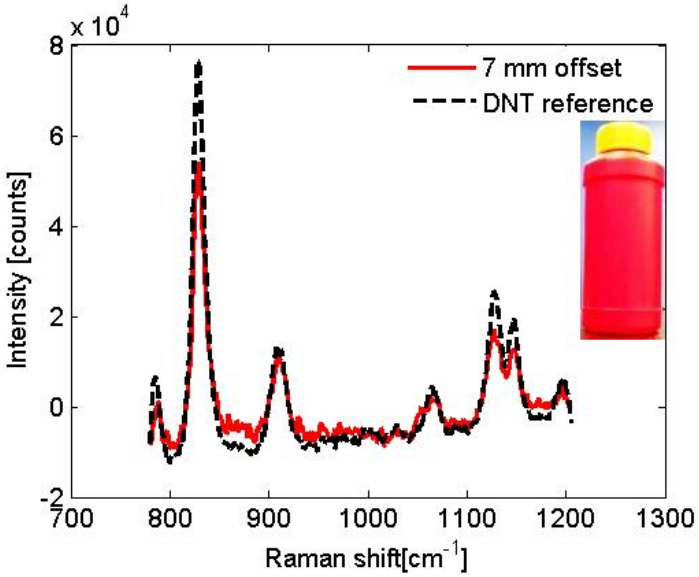

Figure 5 DNT (2, 4-dinitrotoluene) concealed inside a highly fluorescing plastic container detected by the spectrometer.

In this measurement the efficient synchronization between triggering the laser pulse and the detector gate allowed for the significant rejection of the surface layer Raman and fluorescence photons at the optimum gate delay. The depth profiling using a nanosecond pulsed laser can be explained based on refractive index, sample depth and photon migration rates. The delay created by a sample depth of 50 mm of barium sulphate and other solid samples in our measurements were calculated to be greater than 5 nanoseconds[2].

The reliability of the nanosecond system was further consolidated by making a measurement to detect hydrogen peroxide concealed inside white as well as a highly fluorescing plastic container. Hydrogen peroxide is a common explosive precursor and has weak Raman scattering properties when compared to ammonium nitrate and DNT. The TR-SORS results are indicated in figure 6. The Raman spectra of hydrogen peroxide 30% seems to be noisy compared to that of other solid explosive precursors tested, however identification of the substance is possible even inside a highly fluorescing coloured container. The absence any spectral peaks from the container in Figure 6 indicates the possibility of screening weak Raman scatters using the developed spectrometer.

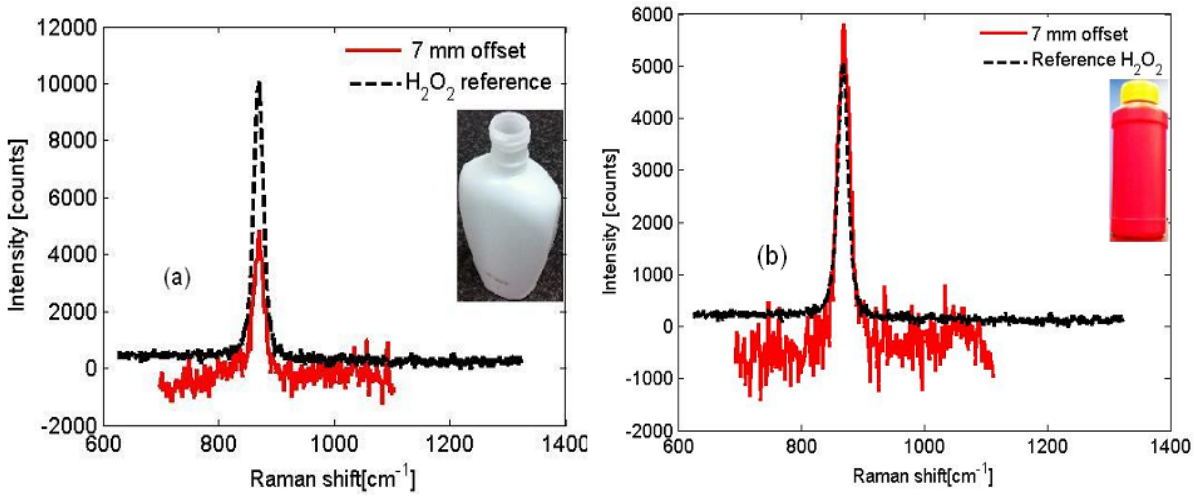

Figure 6 Hydrogen peroxide 30% detected inside a diffuse white (a) and highly fluorescing red (b) plastic container.

4. CONCLUSION

We have presented a Raman spectrometer which employs a combination of the space and time resolved techniques to identify concealed chemical hazards inside diffuse opaque containers. The spectrometer can detect concealed hazards with a single spectral measurement without the requirement of any chemometric for data treatment. A number of explosive precursors were detected inside diffuse opaque containers with excellent signal quality. These results indicate the robustness of the instrumentation to be used in forensic and homeland security applications for the rapid identification of concealed chemical hazards.

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